

Enrichment of nuclear spin isomers by molecular coherent control

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Enrichment of nuclear spin isomers of molecules by infrared radiation resonant to molecular rovibrational transition is considered. Special attention is given to the enrichment by light-induced crossing of far separated ortho and para states.

INTRODUCTION

Nuclear spin isomers were discovered in the late 1920s when ortho and para H_2 were separated by deep cooling of hydrogen gas [1]. This technique was successful because of extremely large gap between the ortho and para states in H_2 . Investigations of heavier isomers were not possible to perform until recently because of the lack of appropriate enrichment methods. First separation of heavy molecules (CH_3F) was achieved using the Light-Induce Drift effect [2]. Later, the isomers of H_2O [3], H_2CO [4], Li_2 [5], and C_2H_4 [6] were enriched. A few practical applications of spin isomer are already known. For example, isomers can affect chemical reactions [7, 8], can significantly enhance NMR signals [9, 10], or can be used as spin labels in NMR based techniques.

Further investigations of nuclear spin isomers and progress in their applications need new enrichment methods. This is rather difficult and challenging task because physical and chemical properties of spin isomers are almost identical. Recently new approach to the isomer enrichment based on molecular excitation by strong electromagnetic field was proposed [11, 12, 13, 14]. In this paper we discuss the isomer enrichment based on the coherent control by strong infrared radiation. We make emphasis on the conditions necessary for the experimental observation of the phenomenon.

LEVEL SCHEME

The level scheme is shown in Fig. 1. We assume that test molecules have only two nuclear spin states, ortho and para. This is very often the case, e.g., in CH_3F [15, 16]. Each of the two vibrational states (ground and excited) has one ortho-para level pair mixed by intramolecular perturbation. Molecules are embedded into a “nonmagnetic” gaseous environment characterized by zero cross-section for collisional ortho-para transition. The infrared radiation is resonant to the rovibrational transition $m - n$ of the ortho molecules.

The molecular Hamiltonian in our problem consists of four terms,

$$\hat{H} = \hat{H}_0 + \hbar \hat{H}_{rad} + \hbar \hat{V} + \hbar \hat{V}'. \quad (1)$$

The main part, \hat{H}_0 , has the eigen ortho and para states shown in Fig. 1. $\hbar \hat{H}_{rad}$ describes the molecular interactions with the external radiation that will be taken in the form of monochromatic travelling wave,

$$\hat{H}_{rad} = -2\hat{G} \cos(\omega_L t - \mathbf{k}\mathbf{r}); \quad \hat{G} = \mathbf{E}_0 \hat{\mathbf{d}} / 2\hbar, \quad (2)$$

where \mathbf{E}_0 ; ω_L and \mathbf{k} are the amplitude, frequency and wave vector of the electromagnetic wave, respectively; $\hat{\mathbf{d}}$ is the molecular electric dipole moment operator. \hat{V} and \hat{V}' are the intramolecular perturbations that mix the ortho and para states in excited and ground vibrational states, respectively. These perturbations originate from the nuclear spin-spin and spin-rotation interactions [17, 18, 19, 20].

Suppose that a test molecule is placed initially in the ortho subspace of the ground vibrational state. Due to collisions the molecule will undergo fast rotational and velocity relaxation *inside* the ortho subspace. This will proceed until the molecule jumps to the state m' , which is mixed with the para state k' by the intramolecular perturbation \hat{V}' (see Fig. 1), or to the state n which is mixed with the para state k by the combined action of the external field and intramolecular perturbation \hat{V} . Admixture of a para state implies that the next collision can move the molecule to another para states and thus localize it inside the para subspace. The spin conversion occurs.

The molecular center-of-mass motion affects the process because of the Doppler effect. Vibrational degree of freedom plays an important role too. After ortho-para transition in

upper vibrational state the molecule relaxes to the ground vibrational state. Consequently, back conversion can only occur through the unperturbed $m' - k'$ channel. It is essential that conversion through the $m - k$ channel can be substantially affected by electromagnetic radiation.

Quantitative description of the isomer conversion can be done using the perturbation theory [21]. The zeroth-order theory neglects the intramolecular ortho-para state mixing by \hat{V} and \hat{V}' and thus contains no ortho-para conversion. In this approximation an external field does not affect the population of para states. The populations of ortho states in the model of strong collisions read,

$$\begin{aligned}\rho_o(e, j, \mathbf{v}) &= \rho_o \{p(\Omega) \tau_{ev} w_j f(\mathbf{v}) + p(\Omega, \mathbf{v}) [\tau_{et} w_j + \tau_e \delta_{jm}]\}, \\ \rho_o(g, j, \mathbf{v}) &= \rho_o w_j f(\mathbf{v}) - \rho_o \{p(\Omega) \tau_{gv} w_j f(\mathbf{v}) + p(\Omega, \mathbf{v}) [\tau_{gt} w_j + \tau_g \delta_{jn}]\}.\end{aligned}\quad (3)$$

Here ρ_o is the total concentration of ortho molecules; e, g designate the excited and ground vibrational states, respectively; j is the rotational quantum number; w_j is the Boltzmann distribution; $f(\mathbf{v})$ is the Maxwell distribution and \mathbf{v} is the molecular center-of-mass velocity. The level populations in Eq. (3) are split into the terms nonequilibrium in j and \mathbf{v} , nonequilibrium only in \mathbf{v} , and equilibrium in j and \mathbf{v} . The magnitudes of these terms are proportional to specific relaxation parameters τ 's (see Ref. [21] for more details). The function $p(\Omega, \mathbf{v})$ is the excitation probability of molecules with particular velocity \mathbf{v} and $p(\Omega) = \int p(\Omega, \mathbf{v}) d\mathbf{v}$,

$$\begin{aligned}Y(\Omega) &= \int \frac{\Gamma_B^2 f(\mathbf{v}) d\mathbf{v}}{\Gamma_B^2 + (\Omega - \mathbf{k}\mathbf{v})^2}, \\ p(\Omega) &= \frac{w_n}{\tau_1} \frac{Y(\Omega)}{1 + \kappa^{-1} + Y(\Omega) \tau_2 \tau_1^{-1}}, \quad p(\Omega, \mathbf{v}) = \frac{p(\Omega)}{Y(\Omega)} \frac{\Gamma_B^2 f(\mathbf{v})}{\Gamma_B^2 + (\Omega - \mathbf{k}\mathbf{v})^2}.\end{aligned}\quad (4)$$

Here $\Omega = \omega_L - \omega$ and $\omega \equiv \omega_{mk}$ is the gap between the states m and k . The function $p(\Omega)$ is the Voigt profile of the absorption line having the homogeneous linewidth $\Gamma_B = \Gamma \sqrt{1 + \kappa}$, where κ is the saturation parameter, $\kappa = 2|G|^2 \tau_1 \Gamma^{-1}$; $|G| = E_0 |d_{mn}| / 2\hbar$ is the Rabi frequency; Γ is the collisional linewidth of the absorbing transition; $\tau_1 = \tau_{et} w_m + \tau_{gt} w_n + \tau_e + \tau_g$ and $\tau_2 = \tau_{ev} w_m + \tau_{gv} w_n$.

In addition to the level population change, an external radiation creates a coherence

(off-diagonal density matrix element) on the $m - n$ transition,

$$\rho_o(n|m; \mathbf{v}) = -i\rho_o \frac{p(\Omega, \mathbf{v})}{2G\Gamma} [\Gamma - i(\Omega - \mathbf{k}\mathbf{v})] e^{i(\Omega t - \mathbf{k}\mathbf{r})}. \quad (5)$$

ENRICHMENT

The first-order theory takes the intramolecular perturbations \hat{V} and \hat{V}' into account. In this approximation the spin conversion appears and it can be affected by the radiation. An external radiation changes the concentration of ortho molecules from the equilibrium value, $\rho_o(0)$, to the steady-state value, $\bar{\rho}_o$. Because the total concentration of the test molecules is conserved, one has steady-state enrichment of para molecules [21],

$$\beta \equiv \frac{\bar{\rho}_p}{\rho_p(0)} - 1 = 1 - \frac{\gamma_{free}}{\gamma}, \quad \gamma = \gamma_{free} - \gamma'_n + \gamma_n + \gamma_{coh}. \quad (6)$$

Here an equal concentrations of ortho and para molecules in equilibrium gas has been assumed that, implies $w_{m'} = w_{k'}$. The conversion rate γ has four terms of different origin. The first one,

$$\gamma_{free} = \frac{2\Gamma|V'|^2}{\Gamma^2 + \omega'^2} [w_{k'} + w_{m'}], \quad (7)$$

is the conversion rate without an external electromagnetic field; $\omega' \equiv \omega_{m'k'}$ is the gap between the states m' and k' . One can see from Eq. (6) that the light-induced enrichment is enhanced by small γ_{free} . The second term is due to the light-induced level depopulation in the ground vibrational state,

$$\gamma'_n = \frac{2\Gamma|V'|^2}{\Gamma^2 + \omega'^2} p(\Omega) w_{m'} (\tau_{gv} + \tau_{gt}) = \frac{1}{2} \gamma_{free} p(\Omega) (\tau_{gv} + \tau_{gt}). \quad (8)$$

The last two terms in γ is convenient to present in a form that can be easily obtained from [21]. The “noncoherent” contribution to the rate,

$$\gamma_n = \frac{2\Gamma|V|^2}{\Gamma^2 + \omega^2} p(\Omega) \tau + 2|V|^2 \text{Re} \left(1 - \frac{\Gamma_1 + i\omega_1}{\Gamma + i\omega} \right) \int \frac{\rho_o^{-1} \rho_o(e, m, \mathbf{v}) d\mathbf{v}}{\Gamma_1 + i(\Omega + \omega_1 - \mathbf{k}\mathbf{v})}. \quad (9)$$

Here $\tau = \tau_{ev} w_m + \tau_{et} w_m + \tau_e$. The “coherent” part, γ_{coh} , originates from the light-induced coherence (5),

$$\gamma_{coh} = -\frac{|V|^2 p(\Omega)}{\Gamma^2 + \omega^2} + \frac{|V|^2}{\Gamma} \text{Re} \frac{\Gamma + \Gamma_1 + i\omega_1}{\Gamma + i\omega} \int \frac{p(\Omega, \mathbf{v}) d\mathbf{v}}{\Gamma_1 + i(\Omega + \omega_1 - \mathbf{k}\mathbf{v})}. \quad (10)$$

The new homogeneous width, Γ_1 , and the ortho-para level gap, ω_1 , are

$$\Gamma_1 = \Gamma \left(1 + \frac{|G|^2}{\Gamma^2 + \omega^2} \right), \quad \omega_1 = \omega \left(1 - \frac{|G|^2}{\Gamma^2 + \omega^2} \right). \quad (11)$$

One can see from Eqs. (8), (9), and (10) that the conversion rate, γ , has two peaks. The peak at the absorption line center ($\Omega = 0$) appears because the excitation probabilities, $p(\Omega)$ and $p(\Omega, \mathbf{v})$, have maximum at $\Omega = 0$. The homogeneous width of this peak is equal to Γ_B that can be very large in molecular systems due to the slow rotational, velocity, and vibrational relaxations. The peak at $\Omega = -\omega_1$ is due to the light-induced crossing of m and k states (see Ref. [13, 14, 21]) and appears formally because of the resonant denominators in the integrands in Eq. (9) and (10). The homogeneous width of the peak at $\Omega = -\omega_1$ is equal to Γ_1 .

Coherent control allows to achieve substantial enrichment if the mixing in ground and vibrationally excited states has the same order of magnitude [21]. On the other hand, close coincidences between ortho and para states in molecules are rather rare. Consequently, such close level pairs in excited vibrational state may be absent, or they cannot be accessible by the available radiation. Below we estimate the enrichment in the case of large ortho-para gap in excited state, $\omega \gg kv_0 \gg \Gamma$, where kv_0 is the Doppler parameter and v_0 is the molecular thermal velocity, $v_0 = \sqrt{2k_B T/M}$. For moderate radiation intensities, $|G| \ll \omega$, the field-dependent terms at the absorption line center, $\Omega = 0$, are

$$\gamma'_n(0) \simeq 0.5\gamma_{free}p(0)(\tau_{gv} + \tau_{gt}); \quad \gamma_n(0) \simeq \frac{2|V|^2}{\omega^2}p(0)\tau\Gamma; \quad \gamma_{coh}(0) \simeq -\frac{|V|^2}{\omega^2}p(0). \quad (12)$$

The terms $\gamma_n(0)$ and $\gamma_{coh}(0)$ have the “off-resonant” nature which manifests itself by the large ortho-para gap, ω , in the denominators. At large ω , the conversion rate, $\gamma(0)$, is determined mainly by $\gamma'_n(0)$ and the radiation depletes the para molecules,

$$\beta(0) \simeq -0.5p(0)(\tau_{gv} + \tau_{gt}). \quad (13)$$

This is analogous to the enrichment by light-induced population change [11, 12]. Maximum of $\beta(0)$ is achieved at sufficiently strong field, $\Gamma_B \gg kv_0$. In this case, $Y(0) \simeq 1$, $p(0) \simeq w_n/(\tau_1 + \tau_2)$ and enrichment reaches the value,

$$\beta_{max}(0) \simeq -w_n \frac{\tau_{gv} + \tau_{gt}}{\tau_1 + \tau_2}. \quad (14)$$

Depending on the relaxation scheme and the origin of the relaxation “bottle neck”, one can achieve different level of enrichment. In the most favorable situation of fast velocity and rotational relaxations the enrichment reaches $-1/4$.

Larger enrichment can be achieved at the level-crossing resonance. The field-dependent rates at the $\Omega = -\omega_1$ can be readily estimated if $\Gamma_B \gg kv_0$. In this case $p(-\omega_1, \mathbf{v}) \simeq p(-\omega_1)f(\mathbf{v})$ and one has,

$$\begin{aligned}\gamma'_n(-\omega_1) &\simeq 0.5\gamma_{free}p(-\omega_1)(\tau_{gv} + \tau_{gt}), \\ \gamma_n(-\omega_1) &\simeq \frac{2\sqrt{\pi}|V|^2}{kv_0}\frac{|G|^2}{\omega^2}p(-\omega_1)\tau, \quad \gamma_{coh}(-\omega_1) \simeq \frac{\sqrt{\pi}|V|^2}{kv_0}p(-\omega_1)\Gamma^{-1}.\end{aligned}\quad (15)$$

The terms, $\gamma_n(-\omega_1)$ and $\gamma_{coh}(-\omega_1)$ are due to the light-induced crossing of the m and k states that has an efficient width equal $kv_0/\sqrt{\pi}$ (compare with the level crossing in molecules being at rest [14]). The main contribution to $\gamma(-\omega_1)$ comes from $\gamma_{coh}(-\omega_1)$ if $|G| \ll \omega$.

The results (12) and (15) allows to determine which peak, $\Omega = 0$, or $\Omega = -\omega$, should be used for enrichment. At low radiation intensity larger enrichment is achieved at $\Omega = 0$ because $p(0) \gg p(-\omega_1)$ if $\Gamma_B \ll \omega$. If radiation intensity is high, $\Gamma_B \sim \omega$, larger enrichment is obtained at $\Omega = -\omega_1$. The ratio of the two peaks reads,

$$\frac{\gamma(-\omega_1)}{\gamma(0)} \simeq \frac{\gamma_{coh}(-\omega_1)}{\gamma'_n(0)} \sim \frac{2\sqrt{\pi}|V|^2}{\gamma_{free}kv_0}\Gamma^{-1}(\tau_{gv} + \tau_{gt})^{-1}.\quad (16)$$

The amplitude of the enrichment peak at $\Omega = -\omega_1$ as a function of $|G|$ and various values of ω are shown in Fig. 2. The calculations were done using the exact expressions for the conversion rates, (7)–(10). In this numerical example the following parameters were used [21], $V = 3$ kHz, $V' = 5$ kHz, $\Gamma = 2$ MHz, $\omega' = 130$ MHz, $kv_0 = 30$ MHz; $\tau_1 = 5$ MHz $^{-1}$; $\tau_2 = 1$ MHz $^{-1}$ and all Boltzmann factors equal, $w_m = w_n = w_k = w_{m'} = w_{k'} = 10^{-2}$.

DISCUSSION

Conditions necessary for the experimental observation of the light-induced enrichment are not easy to fulfil. First of all, the field free conversion rate, γ_{free} , of the molecules

under consideration should be low in order to enhance the role of light-induced changes in the total rate, γ . Note that the rate γ_{free} should combine all significant contributions, e.g., caused by the molecular collisions with the walls of the gas container. At present, only in a few rare cases (see the Introduction) the rates γ_{free} are known.

Next task is to determine the target ortho-para level pair in the excited vibrational state. For this, one has to know rather accurately the relative positions of ortho and para states and the intramolecular ortho-para mixing efficiency as well.

Perhaps, the most difficult problem is to find powerful radiation having right frequency. The most promising sources of such radiation are the powerful Free Electron Lasers.

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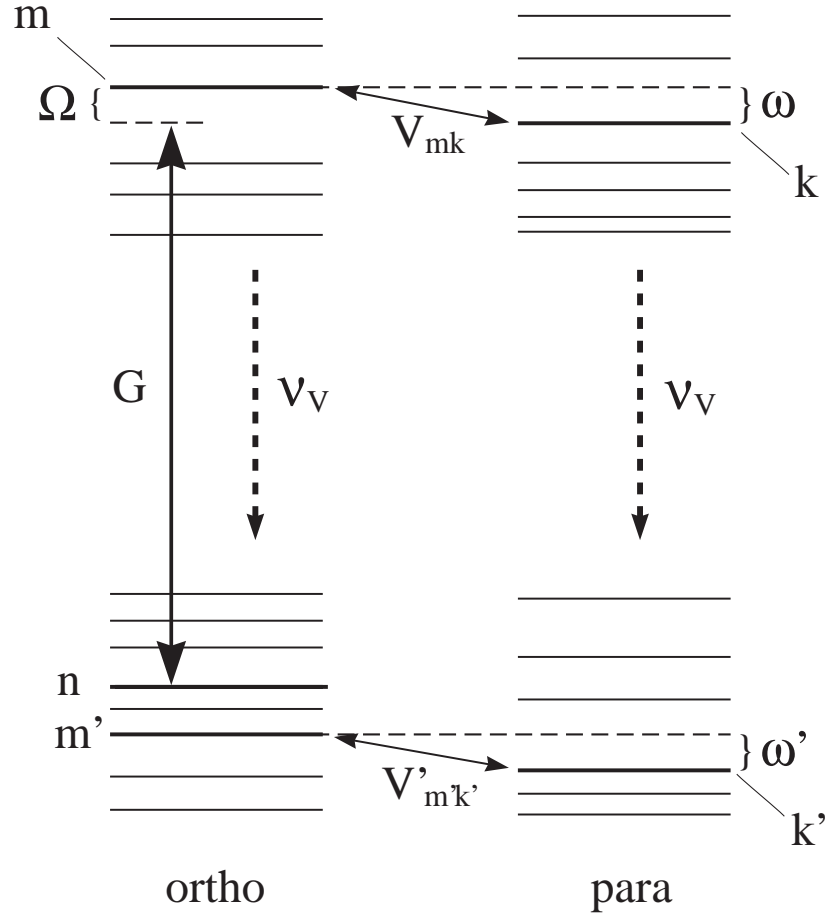


FIG. 1: Level scheme. Vertical solid line indicates infrared excitation. Vibrational relaxation is shown by dashed vertical lines. V and V' indicate the intramolecular ortho-para state mixing.

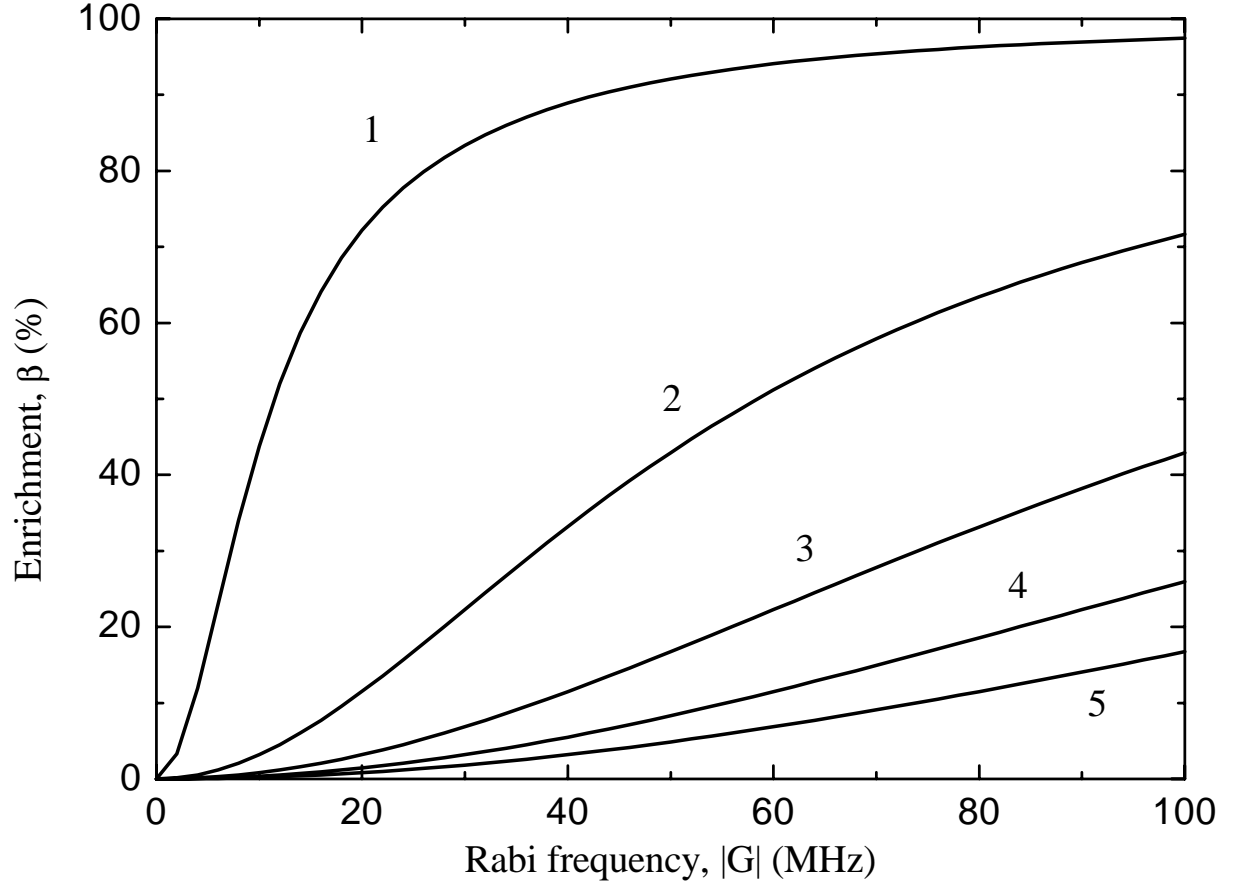


FIG. 2: Enrichment of para molecules as a function of Rabi frequency, $|G|$, and various ortho-para level gaps in excited vibrational state, ω . 1) $\omega = 100$ MHz, 2) 500 MHz, 3) 1000 MHz, 4) 1500 MHz, 5) 2000 MHz.